2.4   Ethylene Hydrogenation

Hydrogenation is certainly the most studied reaction in organic chemical catalysis[24] and it has found numerous applications in organic synthesis in research and industrial processes. Almost all catalytic hydrogenations have been accomplished using heterogeneous catalysts since the earliest stages[25]. The probe reaction chosen for this study is also a hydrogenation, namely, the hydrogenation of ethylene. It is chosen based on the fact that it involves simple molecules, proceeds at ambient temperature and produces only ethane. Thus, the over-all reaction is a simple single-reaction, where $A + B \rightarrow C$. It is one of the most studied reactions[26], since it incorporates the hydrogenation of the simplest possible unsaturated hydrocarbon. Thus, in general, it is expected to be of a simpler nature, and it has been studied extensively with the hope that a full understanding of its chemistry would provide information about the hydrogenation, exchange, dehydrogenation and isomerization of more complicated alkenes[27]. Additionally, since ethylene is of particular importance due to its widespread use as a cheap raw material, and the production of polymer-grade ethylene requires the selective hydrogenation of acetylene, knowledge about ethylene hydrogenation turns out to be important for the minimization of this unselective route[28].

There are various studies on heterogeneous hydrogenation of ethylene, such as: on Pt[27,29–39], on Pd[26,28,40–44] and others[45–52]. Generally, the mechanism proposed by Horiuti and Polanyi[53] in the 1930's is accepted as a reasonable mechanism[54]. In this mechanism, ethylene is adsorbed on the surface by using one of the carbon-carbon double bonds, this is followed by stepwise hydrogenation with atomic hydrogen (formed from dissociatively adsorbed molecular hydrogen) through an ethyl intermediate to form ethane, which is desorbed into the gas phase[27] (see fig.2.2):

Actually, this is only one of the many mechanisms proposed for this reaction. For instance, Farkas and Farkas[38] proposes another mechanism where ethylene is first dehydrogenated before hydrogenation occurs. A third mechanism, proposed by Zaera and Somorjai[34], involves the intermolecular hydro-
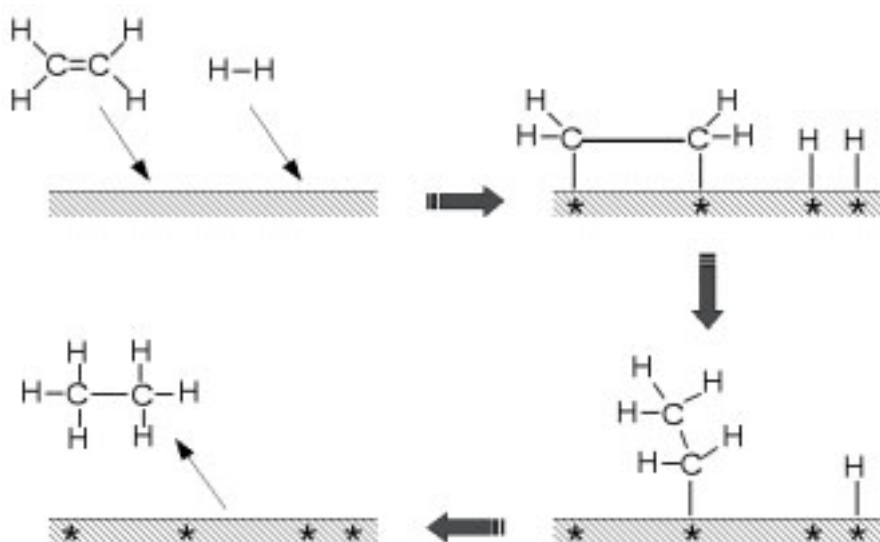
Figure 2.2: A simple representation of Horiuti-Polanyi mechanism.

gen transfer from surface ethylidyne to co-adsorbed ethylene intermediates.

In fact, being one of the fastest heterogeneous catalytic reactions, the hydrogenation of ethylene is a deceptively simple reaction; it posseses an extremely rich and complicated chemistry[27]. For example, Cortright *et al.*[39] reports about the dependence of reaction orders on temperature and partial pressures, and proposed that a combination of different reaction pathways might describe the behaviour; Heese[37] gives experimental evidence about the oscillatory behaviour of the reaction and focuses on the possible complex surface phenomena that may be behind it. Consequently, it can be said that despite its simple structure, ethylene hydrogenation is a challenging reaction system.

2.5   Experimental Reactors

Collection of different kind of information is aimed in the study of catalysts and reactions. The most common goals can be listed as the comparison of different catalysts for a given reaction, the evaluation of reaction kinetics, the evaluation of the sensitivity of catalyst to possible poisons, the testing of catalyst durability and regenarability[55,56]. Particularly speaking, two types of laboratory reactors for two different aims were utilized in this work: a

turbo-reactor for kinetic measurements and a single-pellet reactor for the study of the effect of the pore structure for the given probe reaction.
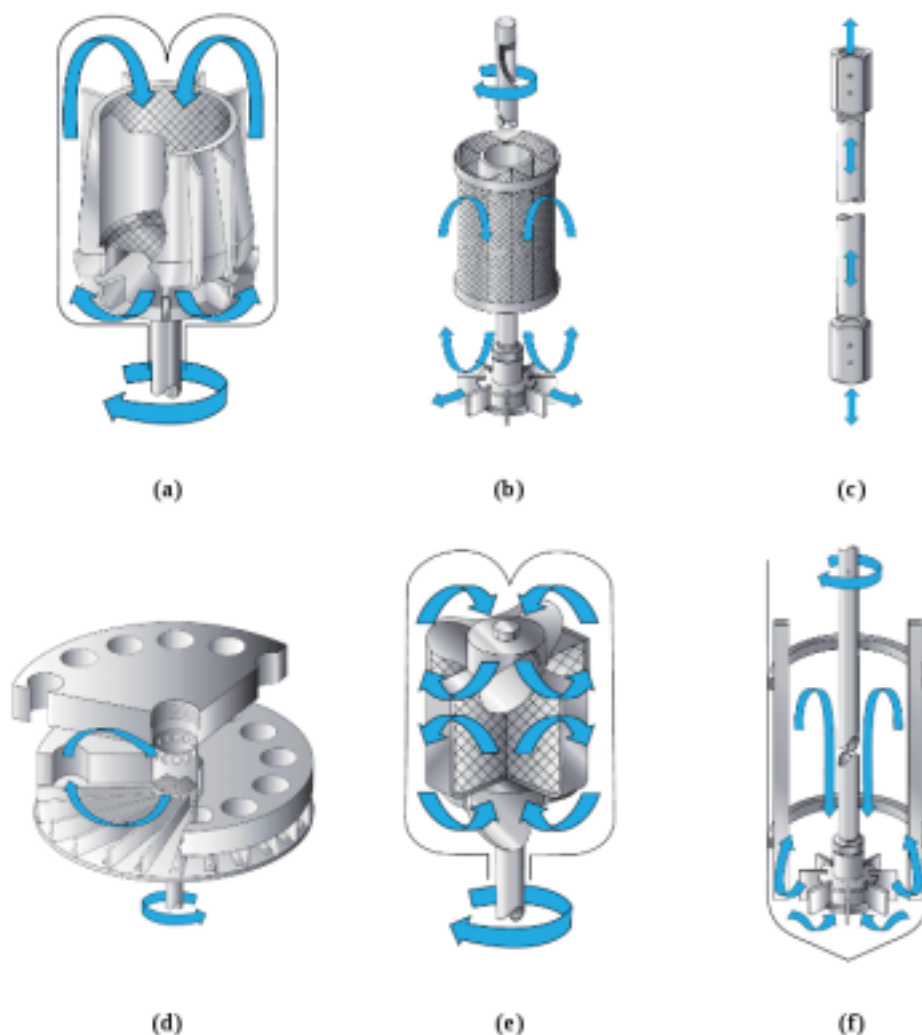
2.5.1 Kinetic Measurement Reactors

Figure 2.3: Common types of reactors used in catalytic research[57]. a) Berty reactor, b) Harshaw falling basket reactor, c) fixed bed (tubular) reactor, d) Caldwell reactor, e) Carberry spinning basker reactor, f) stirred (batch) reactor.

There are various types of reactors that can be used in catalytic research. In fig.2.3, some common types of these reactors can be seen. In general, it can be said that the reactors for kinetic studies are designed to perform like ideal-batch reactor, or ideal-flow reactors, PFR (plug flow reactor) or CSTR (contunious stirred tank reactor), due to the ease of analysis. Also other

categorizations may be made based on the prevailing concentration profile inside the reactors, *differential reactors* that lead to only small conversion, and *integral reactors* that show large conversions alongside them; or based on the mixing/recycling of gas, *internal* or *external recycling.*

An ideal-batch reactor is preferred for rather slow reactions, it is assumed to be perfectly mixed, i.e., it has no concentration or temperature gradients. It gives data with respect to time, i.e., it is under unsteady-state operation. The definition of $t = 0$ for such reactors can be said to be hard in general.

An ideal plug-flow reactor can be operated at steady-state, but the concentrations change along the reactor length and the data is usually taken at the exit. The assumptions for such a reactor are: no concentration gradient in radial direction, no diffusive flow parallel to flow direction and that there exists a plug flow inside. If it is used as an integral reactor, where the conversions are large, concentrations of the intermediates at the exit may be too low for detection. In such a case, spatial probing can be a solution.

An ideal CSTR configuration is also used often and is very valuable for kinetic studies in heterogeneous catalysis. The assumption behind this type of reactor is also the concentration (and temperature) homogeneity inside it. Basically, it can be viewed as an ideal-batch reactor connected to continuous inlet and outlet flows, and thus can achieve steady-state operation. At steady-state, it can be described by the simplest mathematical model since concentrations and temperature depend neither on coordinate, nor on time.

General information and more details about laboratory reactors can be found, for example, in Forni[58] and from AutoclaveEngineers[57].

In this work, the kinetic measurements are performed using a patented[59] turbo-jet reactor. It is an internal-recycle reactor which is constructed to give good mixing even at low gas densities, and operates practically under ideal CSTR-behaviour[60].

2.5.2 Single-Pellet Reactor

The so called *single-pellet reactor* is the type of reactor with which the center concentration of a catalyst pellet can be measured. It consists of two chambers that are separated from each other by a porous catalyst block. The name "single-pellet", literally, could give the impression that the whole block is made up of porous catalyst or that there should exist only a (large) single pellet embedded into a pellet-holder plate separating the two sides. But actually, the reactor could also function with a plate containing many (parallel) (smaller) pellets of the same kind. Thus, the name should be taken to represent the idea of the set-up, not the number of pellets used in it.
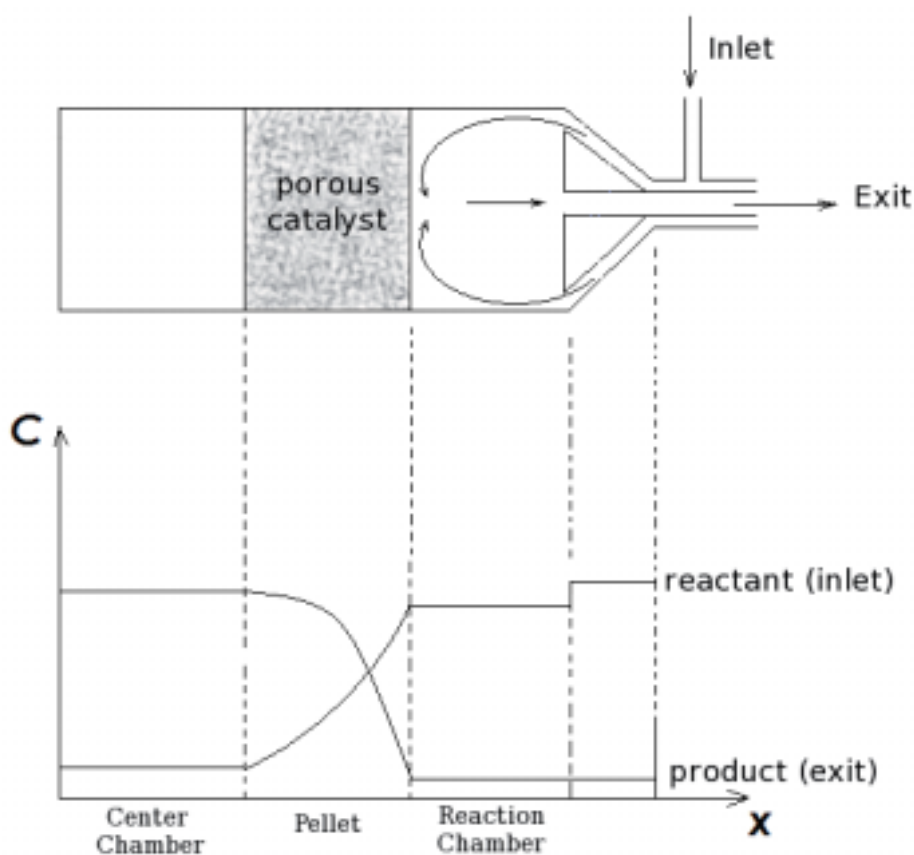

Figure 2.4: Simple scheme of a single-pellet reactor with sample concetration profile inside.

The construction of the reactor is such that one of the two chambers has both inlet and outlet flows connected to it, and the other one has no flow, i.e., a closed-chamber. Since the connection between these two chambers are through the catalyst (pores) only, a concentration profile builds up inside the

catalyst and the two chambers accordingly. At steady-state, the concentration in the closed-chamber corresponds to the concentration at the center of a two times longer catalyst pellet. That is why the concentration measured at the closed-chamber is named as the *center concentration*. A pictorial representation of a single-pellet reactor and the concentration profile inside are given in fig.2.4.

Maybe the first studies with such a reactor configuraiton, one that enables center concentration determination, is done by Roiter *et al.*[61] at 1950's. A closed chamber version is but used later in 1960's by Balder and Petersen[62]. Moreover, a single-pellet reactor utilizing a small infra-red cell is designed by Hegedus and Petersen[63], and the determination of the center chamber concentration without sample taking had become possible. A summary of the theory and applications of the single-pellet (diffusion) reactor can be found in the work of Hegedus and Petersen[64]. More recent studies also present the various applications of this reactor in scientific research, see e.g., Dogu *et al.*[65], Au *et al.*[66], Cabbar *et al.*[67], Dogu *et al.*[68], Nett-Carrington and Herz[69].

A single-pellet reactor is also utilized in this work. It is succesfully used to determine the reaction rate and the center concentrations for catalyst pellets with different pore structures under the same operating conditions.